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(19) (CA) **CANADIAN PATENT** (12)

(54) REACTOR ELECTRODE WITH POROUS PORTION AND TITANIUM
PORTION

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Canada

ABSTRACT OF THE DISCLOSURE

An electrode is provided for use in treating waste water containing metallic species. The electrode permits plating in the cathodic mode and stripping in the anodic mode. The electrode includes a material, preferably titanium, which exhibits a sudden change in electrical characteristics after stripping and this change can be used to sense the end of stripping thereby minimizing attack on the electrode. A reactor and method are also disclosed.

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This invention relates to apparatus and to processes for use in cathodic extraction of selected ionic species from liquid waste and more particularly for use in extracting small concentrations of such species from waste waters both to meet environmental standards and to make it possible to recycle the waste water to provide closed loop continuous processes.

10 Stated generally the present invention is directed to improving the quality of waste water. New environmental standards are being promulgated in many countries making it necessary to treat waste waters to reduce the concentration of toxic ingredients to very low levels before discharging to publically owned waste treatment plants, water courses, lakes, oceans, etc.

In many commerical processes it would be ideal if waste water treatment could be provided capable of recycling all or a major portion of the treated water continuously to effectively remove the need to discharge effluent. Obviously systems capable of such closed cycle
20 treatment would have to be both economic and extremely reliable to avoid having to suspend the commercial process while the treatment facility is serviced or repaired.

The present invention uses an electrochemical approach to providing apparatus and process for waste water treatment to reduce metal contaminants down to levels of concentration acceptable in the most stringent of promulgated environmental regulations.

It should be noted that for the purposes of the present description, the word "electrochemical" is used
30 throughout to describe apparatus and processes in which an input of electrical power is used to bring about activity

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at a working electrode.

There are two distinct groups of electrochemical processes. The first group of processes have their reaction rates kinetically controlled in that the electrolyte being treated contains high concentrations of electro-active species. One such process is the electro-refining of zinc where there is inherently a high concentration of zinc in the electrolyte. The working electrodes used in such processes are sometimes of the same material as that being stripped so that the resulting product can be used directly, but more commonly the electrode is designed for mechanical stripping. However in some instances the design is dictated by other requirements such as those described in U.S. Patent 3,953,313 to Levenson. In the Levenson structure the prime consideration is that the electrode be combustible so that silver deposited on the electrode can be recovered by melting during combustion.

A second group of electrochemical processes have reaction rates controlled by mass transfer considerations rather than by kinetic requirements. By contrast with electrodes used in kinetically controlled processes, working electrodes used in mass transfer controlled processes must exhibit characteristics which enhance mass transfer rates. One such characteristic is a large surface area to volume ratio. Attempts have been made to achieve acceptable ratios using packed beds of fibrous or granular material as well as active beds which can move in a flow of electrolyte. In all instances these attempts have suffered from distinct disadvantages based primarily on the difficulty of providing a uniform and controlled electrical potential throughout

the electrode to make full use of the surface area. As a result of this major drawback none of these mass controlled processes has achieved significant acceptance.

More recently electrodes and reactors have been described using carbon fibre arrangements both to provide a large surface area to volume ratio and to limit fluctuation in electrical potential throughout the electrode. Such electrodes and reactors are described in U.S. Patents 4,046,663 and 4,046,664 which were filed under Convention Priority
10 in the United States on July 28, 1975.

An electrode and reactor have also been proposed on a laboratory scale by D. Yaniv and M. Ariel in an article appearing in the Journal of Electroanalytical Chemistry Volume 79 (1977) pages 159 to 167. The structure taught in this article includes an electrode of graphite cloth positioned in a frame defining an opening having an area of 2.4 cm^2 . The authors state that their results confirm the feasibility of exploiting graphite cloth as a practical electrode material suited for flow-through configurations.
20 However they go on to indicate that although their laboratory reactor worked well, it would be necessary to undertake further work to optimize a reactor using a graphite cloth electrode.

With this background the present invention is directed to such optimization for use in stripping metallic ionic species from waste waters. It has been found that there are in fact numerous factors which must be taken into consideration in designing an electrode using carbon fibres if significant results are to be achieved in mass transfer
30 controlled configurations. One of these factors is (as

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previously mentioned) to provide continuous electrical conductivity throughout the electrode to minimize voltage and current variations. Also, the surface area must be available to electrolyte so that a related consideration is that a maximum surface area to volume ratio be provided in which a high percentage of the surface area is usable. It has been found in practice that for satisfactory results this ratio should exceed $100 \text{ cm}^2/\text{cm}^3$.

10 It is also essential that the flow path be controlled so that the waste water passes through the electrode structure with a minimum of blind or dead-end passages. The effectiveness of the electrode on the waste water will depend upon the efficiency with which the ionic species is brought into proximity with the surface of the electrode to cause deposition on the electrode surface. Ideally the pores between fibres lead one from another defining tortuous paths through the electrode to minimize laminar flow and to encourage the break-up of boundary layers around the surfaces. The average pore size, which is of course related to voidage, 20 should be in the range 0.8 to 3,000 μm and the voidage should be in the range 30 to 99% and preferably 75 to 80% of the total volume of the electrode. Also the effectiveness of the electrode requires that 80% of the pores should lie in the range 1 to 100 μm , and preferably in the range 1 to 50 μm . It will of course be appreciated that an even distribution of similar pores is desirable for reasons of flow equalization.

In order to maintain an electrode structure having the above characteristics, it is necessary to restrain 30 fibres within the electrode and to use a feeder electrode having very low electrical resistance for improved current distribution. In some constructions the fibres are similar to yarn rather than thread and each yarn is made up of many

smaller fibres. An example of a suitable material would be a woven cloth made up of carbon fibre yarn which is spun quite loosely but woven quite tightly. As a result larger spaces between adjacent yarns will be minimized while the elements or fibres making up the yarn will be free to move slightly in the flow of electrolyte while being controlled by the restraint to maintain the pore size required and the pore size distribution necessary.

10 One approach to providing the electrode for use in a mass transfer arrangement is to be found in Japanese patent 67267/76 which was published on June 10, 1976 naming Mitsui Petrochemical Industries Ltd. as owner. This patent teaches the use of a composite electrode having a carbon fibre material in contact with a feeder which may be of several different metals, some of which are coated. Such electrodes may have good characteristics when used simply as a working cathode. However the problem of recovery of metal from such an electrode has not been solved.

20 The present invention is directed to an electrode and reactor which will operate in a mass transfer controlled environment and which will permit cyclic recovery of metallic deposits without undue electrode deterioration. As mentioned earlier with reference to kinetically controlled processes, recovery methods include mechanical stripping and electrode burning. Neither of these methods is acceptable in achieving applicant's desired results. Also, it is possible to use purely chemical stripping processes in some instances and although such processes may prove acceptable in some situations applicant uses polarity reversal to cause current
30 reversal thereby stripping the working cathode of metallic

deposits into solution.

Polarity reversal has of course been used in many forms. However no practical system is known to applicant which both lends itself to automatic cyclic operation in a mass transfer controlled process and yet avoids significant electrode damage during the stripping cycle. This is because the feeder (and sometimes the carbon fibre also) is subject to attack during the anodic stripping cycle, and in some instances the feeder would simply dissolve. The feeder can of course be made of platinum or metal coated with platinum to avoid degradation of the feeder. Such an approach is very expensive and does not solve the problem of anodic attack at the carbon fibres. In fact the problems inherent in stripping by polarity reversal are such that chemical stripping processes are used commercially in preference.

Unexpectedly applicant finds that when titanium is used as the feeder it is advantageous to use polarity reversal for stripping. A coating is formed on the titanium in the anodic mode which can be used to advantage as will be described. The resulting electrode is very durable and is capable of meeting the aforementioned requirements for a mass transfer controlled cathode. The electrode is also extremely advantageous in a polarity reversal stripping cycle making it possible to achieve a commercial and very reliable apparatus and process for treating waste waters containing metallic pollutants.

It is also of interest that the space-time yield of applicant's electrode is outstanding. Space-time yield is a standard indicator of the performance of a heterogenous

catalytic reactor. In electrochemical engineering a convenient measure is the amount of current carried by an electrode at high current efficiencies per unit volume of electrode. This comparative measure of electrode efficiency is used with a given electroactive species having a known concentration and conductivity. It was found that for a copper solution having a concentration of 640 p.p.m. at a current efficiency of 52% the following space-time yields were obtained for different electrodes as shown below.

Reactor Type	Space-Time ₃ yield mA/cm ³
Restrained Packed Bed	57
Fluidized Bed	4 to 60
Filter Press, Capillary gap systems etc.	1 or less
Present electrode	Greater than 1280

It should be noted that at increased flow velocities the present electrode has given space-time yield results as high as 6800 mA/cm³ and at very low flow rates the space-time yield recorded was 500 mA/cm³.

It will be evident from the foregoing that the invention provides a means of extracting metallic pollutants from waste water efficiently. A preferred embodiment of the invention will now be described with reference to the drawings, in which:

Fig. 1 is a perspective view of a preferred embodiment of a reactor according to the invention and including a plurality of individual electrochemical cells

arranged adjacent one another according to a preferred embodiment of the invention;

Fig. 2 is an exploded perspective view of a portion of the reactor shown in Fig. 1 and illustrating parts of the cells;

Fig. 3 is a perspective view with a portion broken away and illustrating a flow divider used in the cells;

Fig. 4 (drawn adjacent Fig. 1) is a sectional top view generally on line 4-4 of Fig. 2 and showing the relationship of parts in adjacent cells after assembly;

Fig. 5 is a diagrammatic representation of a complete apparatus incorporating the reactor; and

Figs. 6 to 8 are graphical representations of results obtained using apparatus similar to that described.

Reference is made first to Fig. 1 which shows the reactor designated generally by the numeral 20 and consisting of a plurality of individual cells 22 arranged for operation in parallel. The cells are restrained between a pair of end plates 24, 26 by long bolts 28 and the parts used to make up the cells are aligned by a pair of bolts 30, 32 which pass through parts of the cells as will be explained. For the purposes of description the reactor 20 will be described in the position shown in Fig. 1 but with suitable venting for gases it can be used in any orientation.

Electrical connection is made through cathode bars 34 provided at both sides of the reactor (one side being shown in Fig. 1) and by anode bars 36 at the top of the reactor. As will be described more fully with reference to Fig. 2, waste water to be treated is fed from behind and at the bottom of the reactor as shown in Fig. 1 and

exits by way of outlet 38. Anolyte is also fed from the bottom of the reactor exiting through a further outlet 40. These outlets are used during the plating or metal removing cycle and afterwards, when deposits on the cathode are to be stripped, the flow of waste water ceases and is replaced by a flow of a suitable electrolyte which again enters from the bottom and behind the reactor and in this case leaves through another outlet 42. As will become evident from further description, the electrolyte is made to back flush through the cathode to provide some mechanical cleaning action as well as an electrochemical removal of the plated metal.

Reference is now made to Fig. 2 to illustrate some of the mechanical details of the reactor shown in Fig. 1 and in particular parts which make up individual cells. As seen in Fig. 2 a cathode frame 44 is positioned for electrochemical action relative to adjacent sides of lead anodes 46, 46'. In effect a complete cell consists of the parts shown in Fig. 2 although only the sides of the anodes facing the cathode frame are active in the cell. Opposite sides of these anodes are active in adjacent cells. except at the ends of the reactor where sides of the lead anodes adjacent the end plates 24, 26 (Fig. 1) will be insulated from these end plates and have no electrochemical effect.

The cathode frame 44 is of moulded polyurethane and contains peripheral conductors 48, which grip a conductive mesh 50 made up of interwoven titanium wires. The peripheral conductors are attached to the external cathode bars 34 (Fig. 4) to

ensure good electrical continuity from the bars to the mesh 50. This mesh is made up of 0.032 inch diameter titanium wire providing 55% open area.

The mesh 50 forms a secondary portion of the cathode and two primary portions are attached one to either side of the mesh. One primary portion can be seen in Fig. 2 and consists of a sheet 52 of carbon fibre cloth sold under the trademark MORGANITE 7401 G and sold by Morganite Modmor Ltd. of England. This sheet is laid in surface-surface contact with the mesh 50 and held in place by a series of staples made of titanium wire and similar to those used in conventional stapling equipment. The staples are not shown in the drawings because of the scale used but are distributed over the sheet 52 where needed to hold the sheet in place. As will be described the edges of the sheets are restrained by applying a pressure against the mesh 50.

The peripheral cathode frame 44 also defines a series of top and bottom openings to transport liquids as indicated with reference to the outlets 40, 42 and 38 of Fig. 1. For instance waste water to be treated enters through central bottom opening 54 where some enters by an inlet 56 into a space adjacent the sheet 52 so that the waste water is provided on the other side of the cathode so that the waste water flows through the cathode and then leaves through an outlet 58 associated with a central top opening 60 before eventually leaving the reactor by way of outlet 38 (Fig. 1). This flow takes place during the treatment of waste water to remove metallic ionic species and subsequently when it is necessary to strip the deposited metal from

cathode sheet 52 and the associated sheet on the other side of the mesh 50, the flow of waste water is discontinued and a stripping electrolyte is made to flow through the cathode. This electrolyte enters by way of a bottom opening 62 and inlet 64 and leaves by way of a top outlet 66 associated with the top opening 68 before finally issuing from outlet 42 (Fig. 1). Here again the flow is through the cathode but in the opposite direction to that taken by the waste water to enhance the flushing action of the stripping electrolyte.

The cathode frame 44 also defines a bottom opening 70 and top opening 72 both of which are used for anolyte and these openings simply provide passage through the frame. There are also two small openings 71, 73 for receiving fitted bolts 30, 32 (Fig. 1) to align the parts as will become apparent.

A flow chamber for the waste water is defined on the inlet side of the cathode partly by space within the frame on this side and by a neoprene gasket 74 adjacent the face of the frame 44 as better seen in Fig. 4. Openings in the gasket are provided in alignment with the openings described with reference to the frame 44, and spacer strips 76 are compressed between the gasket and the face of sheet 52 at the periphery of the sheet. These strips ensure that the sheet 52 is held tightly against the mesh 50 at the edges. The inlet chamber is completed by a diaphragm 78 nipped between the gasket 74 and a further neoprene gasket 80. A similar outlet chamber is provided by similar parts labelled correspondingly using primed reference numerals.

The gasket 80 also provides access for anolyte

into a chamber defined in part by the gasket and also by the diaphragm 78 and lead anode 46. The assembled arrangement is better seen in Fig. 4. The flow of anolyte is facilitated by a pair of moulded flow diverters 82, 84 of polyurethane arranged to fit in the gasket and one of which is better seen in Fig. 3. These diverters ensure that there is access for anolyte into the chamber adjacent the anode 46 for electrochemical continuity between the adjacent surface of the anode and the cathode contained in the frame 44. A pair of small neoprene gasket pieces 86, 88 are shown adjacent the lead plate anode 46 to compensate for the thickness of the anode in the assembly and to ensure continuity of flow for the waste water and the electrolyte used to strip the cathode.

The parts described to the left of the cathode frame as shown in Fig. 2 are duplicated to the right and as mentioned are indicated using primed reference numerals. Apart from the fact that the spacer strips 76' are slightly different because of the arrangement of inlets and outlets in the frame 44, the parts to the right are identical to those described on the left of the frame 44.

It will now be evident from the foregoing description that each cathode is associated with two anodes and that the parts are arranged to define a housing having a waste water flow path through the cathode. Also, during the stripping cycle the flow passes through the cathode in the opposite direction. Electrical distribution is maintained in the cathode by a combination of the mesh 50 and the natural conductivity of the two sheets such as sheet 52. Because the flow is through the structure the

mesh 50 should have sufficient strength to resist flow forces and to prevent any significant distortion. Also, to ensure electrical continuity, the staples used to locate the sheets on the screen should be quite tight to ensure surface-to-surface contacts between the sheets and the mesh.

Reference is next made to Fig. 5 to show the reactor in use in a typical installation. In practice the reactor would be used in parallel or possibly in series with numerous other reactors as necessary to accommodate the volume of effluent being treated. As seen in Fig. 5 the reactor 20 receives waste water input from a pump 90 by way of an inlet 92 and treated waste water leaves by the outlet 38. While waste water is fed to the reactor, anolyte is driven in a closed loop by a pump 94 through an inlet 96 and returns from the reactor by way of the outlet 40. The flow of waste water and anolyte is controlled electrically by a pump control system 98 associated with a power supply control 100 which maintains the current at a predetermined level related to the voltage requirement.

After the cathode has been plated for some time, the pressure drop between the inlet 92 and outlet 38 will change and this is monitored and a signal fed to the pump control system by way of a transducer 102. Once the pressure drop reaches a predetermined value, the pump control system removes power from the pump 90 and causes the power supply control to reverse the polarity of the cathode and anode for stripping. At the same time a pump 104 is energized to feed stripping electrolyte into an inlet 106 which back flushes the cathode and leaves by way of the outlet 42 carrying with it a concentrated solution of the metal being

stripped from the waste water. The stripping cycle continues until a highly resistive coating is formed on the secondary portion of the cathode (now being used as an anode). The power supply control senses this increase in resistance and causes reversal of the polarity and at the same time causes the control system to re-energize the pump 90 and to isolate the pump 104. The coating on the secondary portion of the cathode is then electro-reduced and is again used to plate metal from the waste water. The cycle can be repeated continuously and automatically.

It will be appreciated that it is critical to the life of the working electrode that during the use in an anodic mode, the electrode must not be exposed to high currents at voltages where a significant volume of oxygen (or chlorine if a chloride background is present) would be produced. The life of the electrode is protected by the effect of the titanium feeder or secondary portion of the electrode. After the plated metal has been stripped from the cathode, a highly resistive coating is formed on the titanium rendering the electrode inactive well before significant anodic attack at the primary portion of the electrode. Unexpectedly upon reversing polarity so that the electrode is again cathodic the coating on the titanium is electro-reduced very quickly despite its highly resistive nature when functioning as an anode. The electrode thereby reverts back to its original condition for use again as a low resistance feeder functioning as a cathode.

The exact nature of the coating on the titanium is not understood fully. Chemically induced oxide coatings of titanium are sufficiently resistive to prevent use as an anode. Consequently applicant must presume that although the electrochemically induced coating formed on the titanium feeder is no doubt an oxide, it exhibits an unexpected characteristic which is most desirable in the present application.

Returning to Fig. 5, the pump '94 which drives
10 the anolyte is also connected to the pump control system. Consequently in emergency the pump control system can switch off this and the other pumps and at the same time disengage the power used to drive the reactor.

The apparatus shown diagrammatically in Fig. 5 is particularly useful in stripping nickel from waste water. It has been found that processes of this kind do not require diaphragms such as the diaphragm 78 shown in Fig. 2 but with a diaphragm and proper selection of anolyte, the anode life is enhanced significantly despite some dif-
20 fusion through the diaphragm.

The power supply control described sensed when the secondary portion became highly resistive and this was used as a trigger. Of course the system

can also be controlled by either setting the voltage and monitoring the current requirements or alternatively setting the current and monitoring the voltage requirements.

Figs. 6 to 8 illustrate some of the results obtained with apparatus of the type described. Fig. 6 illustrates the results obtained using a cathode having 79% voidage, average pore size of 18 μm , a pore size distribution of 95% in the range 1 to 100 μm and a surface area to volume ratio of 5,600 cm^2/cm^3 . It will be seen that initially the waste water nickel content was 4,000 parts per million (p.p.m.). After twenty seconds the concentration had diminished to about 2,000 p.p.m. and that subsequently concentrations down to 1 p.p.m. could be obtained in about 120 seconds. Such a small residence time makes the process viable economically. This is an extremely important consideration in any commercial process particularly where the treatment is made necessary by legislation and is not adding to the quality of the finished product being made by the commercial process.

Results are shown for copper in Fig. 7. It will be seen that for fixed residence times of 1.75, 3.45 and 5.15 seconds, the percentage of copper removed from solution approaches 100% in these very short residence times using current densities below 50 mA/cm^2 . In all instances the input had a copper concentration of 180 p.p.m.

Further results are shown in Fig. 8 when applied to the removal of zinc from solution. In Fig. 8 the input was 10 parts per million and the residence time 3 seconds.

It will be seen that the percentage of zinc removed approached 100% when current densities of about 75 mA/cm² were used in this very short residence time.

Figs. 6 to 8 demonstrate the results which can be achieved using this apparatus and process. After the materials have been removed from the waste water, they can be stripped quickly using suitable electrolyte giving an output having high concentrations of the metal being removed. This output can be either used in other processes or stripped
10 electrochemically using a kinetically controlled system. Because the concentrations can be very high, the efficiency of the kinetically controlled system provides no difficulty.

The preferred embodiment described is typical of many forms of apparatus incorporating the invention. The flow arrangement can be varied and in general if the effects of the feeder are paramount, the carbon fibre cloth can be replaced by any other suitable conductive medium. Also the use of any material exhibiting the electrochemical characteristics of titanium is within the scope of the invention. It should
20 also be noted that the feeder may be a plate if the flow is not through the electrode and a perforated sheet can be used in place of the mesh shown in the preferred embodiment. All these and other such variations are within the scope of the invention as described and claimed.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:

an electrically conductive and porous primary portion having a surface area to volume ratio exceeding 100 sq. cm./cu. cm.;

a titanium secondary portion; and

means restraining the primary portion in surface-to-surface mechanical contact with the secondary portion, the secondary portion being adapted to be connected electrically to a power supply for improved electrical potential distribution to the primary portion to enhance plating during removal of the metallic species from the waste water, the secondary portion also causing a sudden change in the electrical requirement of the electrode after stripping in the anodic mode whereby this sudden change in the electrode facilitates automatic control of the reactor used in a repetitive plating and stripping cycle.

2. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:

a carbon fibre cloth having a surface area to volume ratio greater than $100 \text{ cm}^2/\text{cm}^3$, an average pore size in the range 0.8 to 3000 μm with 80% of the pores being in the range 1 to 100 μm , and a voidage of 30 to 99% of the volume of the primary portion;

a titanium feeder including means adapted to be coupled to an electrical supply circuit; and

means restraining the carbon fibre cloth in surface-to-surface mechanical contact with the titanium feeder

to provide an electrode having a space-time yield greater than 500 mA/cm³ whereby the electrode can be stripped automatically using the electrode anodically due to a sudden change in the electrical requirements of the electrode after stripping, this sudden change being caused by a coating on the titanium which may be electro-reduced quickly upon again using the electrode cathodically.

3. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:

a porous primary portion being electrically conductive and having a surface area to volume ratio exceeding 100 sq. cm./cu. cm.;

a titanium secondary portion defining a screen and means adapted to be coupled to an electrical supply circuit; and

means restraining the primary portion in surface-to-surface mechanical contact with the screen to support the primary portion and to define a flow path for electrolyte through the electrode, the secondary portion also providing an improved potential distribution over the primary portion for enhanced plating action while acting as a cathode and causing a sudden change in the electrical requirement of the electrode after stripping while acting as an anode whereby the electrode facilitates automatic control of the reactor used in a repetitive plating and stripping cycle.

4. A reactor for use in removing a metallic species from waste water, the reactor comprising:

means defining a flow path for the waste water;

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a working electrode positioned in the flow path and including a primary portion having an active surface area to volume ratio greater than $100 \text{ cm}^2/\text{cm}^3$, a titanium secondary portion, and means restraining the primary and secondary portions in contact with one another for improved potential distribution in the primary portion;

a secondary electrode spaced from the working electrode;

a power supply control including means for maintaining an electrical circuit with the working electrode as cathode during metal removal, means for maintaining an electrical circuit with the working electrode as anode during metal stripping, means for reversing polarity of the electrodes, means for sensing a change in the electrical requirements immediately after stripping caused by coating of the titanium secondary portion and for activating said polarity reversing means to change the working electrode back to the cathodic mode; and means responsive to electrode loading during plating for activating the polarity reversing means to change the working electrode to the anodic mode to commence stripping.

5. In an electrochemical reactor of the type having a working electrode for use in removing metallic ionic species from waste water, the improvement in which the working electrode is arranged so that the waste water flows through the working electrode during removal of metallic ionic species while it is functioning as a cathode and in which the working electrode comprises: a fibrous primary portion which is electrically

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conductive, has an active surface area to volume ratio greater than $100 \text{ cm}^2/\text{cm}^3$, exhibits an average pore size in the range 0.8 to $3,000 \text{ } \mu\text{m}$ with 80% of the pores being in the range 1 to $100 \text{ } \mu\text{m}$, and has a voidage of 30 to 99% of the volume of the primary portion; and a secondary portion arranged in surface-to-surface contact with the primary portion, the secondary portion being a feeder of titanium metal mesh which combines with the primary portion to provide a substantially constant voltage distribution throughout the working electrode, the secondary portion developing a highly resistive oxide coating after stripping the metal from the electrode while functioning as an anode so that a signal can be developed in the electrical supply to the reactor to indicate that stripping is completed thereby minimising anodic attack on the primary portion of the electrode.

6. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:

an electrically conductive and porous primary portion and having a surface area to volume ratio exceeding $100 \text{ sq. cm./cu. cm.}$;

a secondary portion of a material which produces a highly resistive coating when used as an anode, which coating is readily electro-reduced when used as a cathode;

means restraining the primary portion in surface-to-surface mechanical contact with the secondary portion, the secondary portion being adapted to be connected electrically to a power supply for improved electrical potential distribution to the primary portion to enhance plating during removal of the metallic species from the waste water, the secondary portion

also causing a sudden change in the electrical requirement of the electrode after stripping while functioning as an anode whereby this sudden change in the electrode facilitates automatic control of the reactor used in a repetitive plating and stripping cycle.

7. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:

a carbon fibre cloth having a surface area to volume ratio greater than $100 \text{ cm}^2/\text{cm}^3$, an average pore size in the range 0.8 to $3000 \mu\text{m}$ with 80% of the pores being in the range 1 to $100 \mu\text{m}$, and a voidage of 30 to 99% of the volume of the primary portion;

a feeder of a material which produces a highly resistive coating when used as an anode, which coating is readily electro-reduced when used as a cathode and which includes means adapted to be coupled to an electrical supply circuit; and

means restraining the carbon fibre cloth in surface-to-surface mechanical contact with the feeder to provide an electrode having a space-time yield greater than $500 \text{ mA}/\text{cm}^3$ whereby the electrode can be stripped automatically using the electrode anodically due to a sudden change in the electrical requirements of the electrode after stripping, this sudden change being caused by the coating on the feeder which is electro-reduced quickly upon again using the electrode cathodically.

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8. An electrode for a reactor used to treat waste water containing a metallic species, the electrode comprising:
a porous primary portion being electrically conductive and having a surface area to volume ratio exceeding 100 sq. cm./cu. cm.;

a secondary portion of a material producing a highly resistive coating when used as an anode, which coating is readily electro-reduced when used as a cathode and defining a screen, and means adapted to be coupled to an electrical supply circuit; and

means restraining the primary portion in surface-to-surface mechanical contact with the screen to support the primary portion and to define a flow path for electrolyte through the electrode, the secondary portion also providing an improved potential distribution over the primary portion for enhanced plating action in the cathodic mode and causing a sudden change in the electrical requirement of the electrode after stripping while functioning as an anode whereby the electrode facilitates automatic control of the reactor used in a repetitive plating and stripping cycle.



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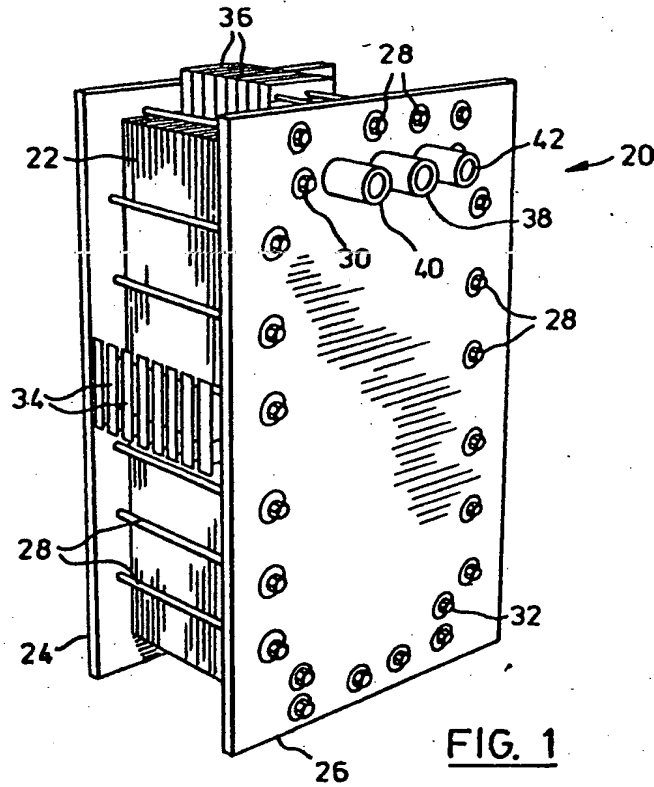


FIG. 1

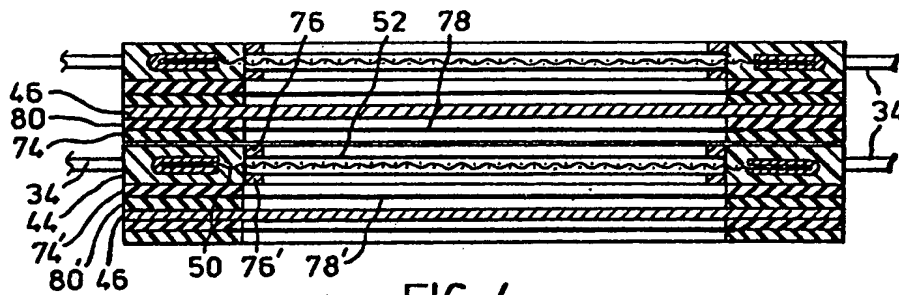


FIG. 4

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Wills, Rogers & Co

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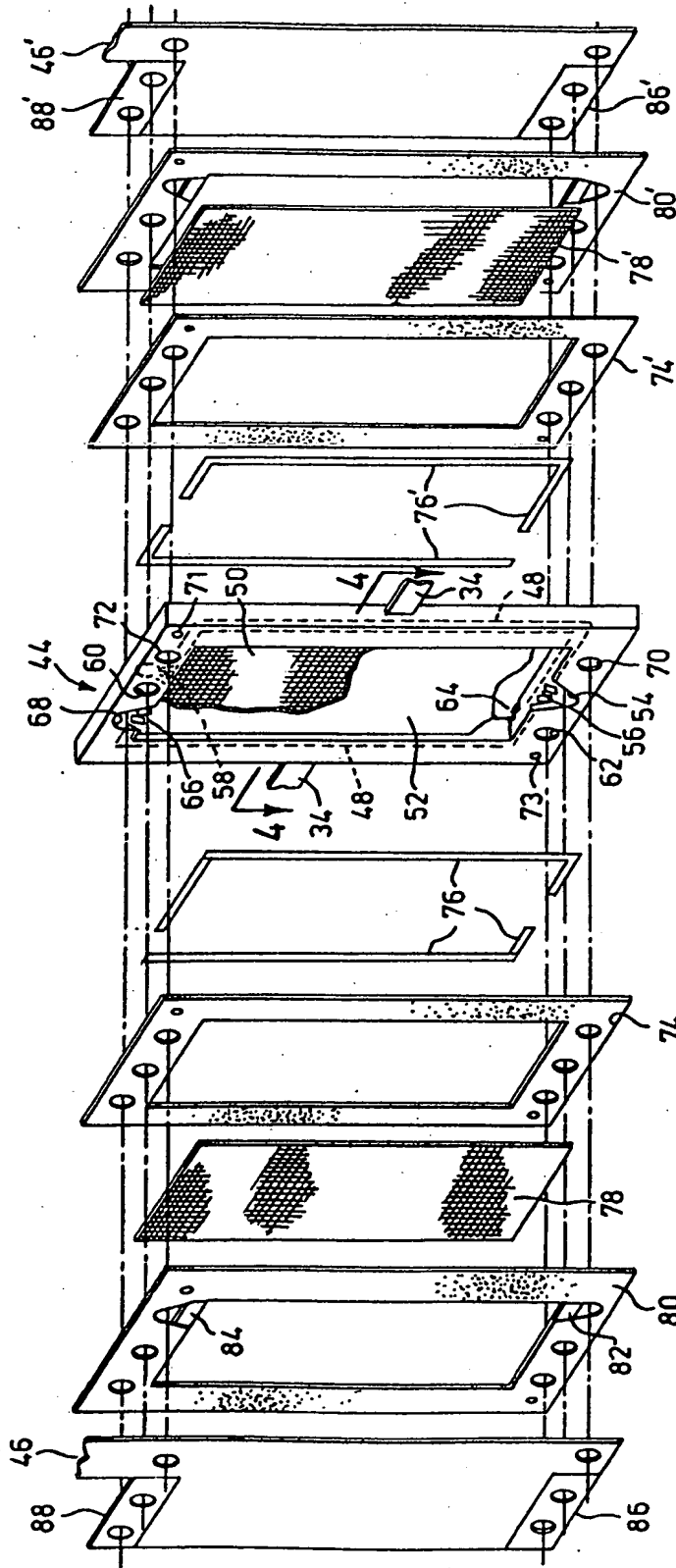


FIG. 2

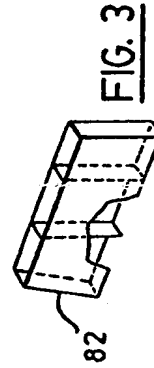
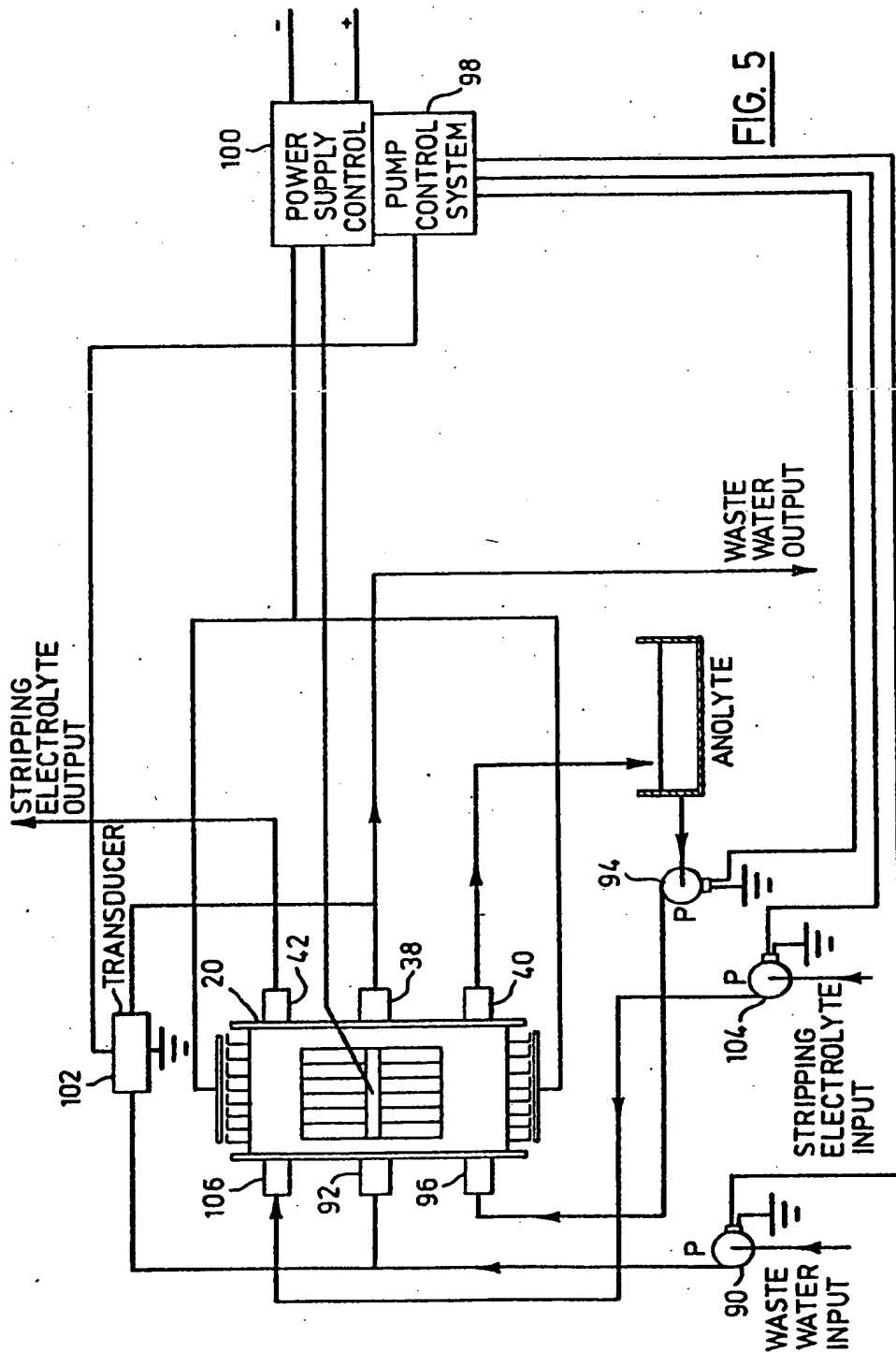


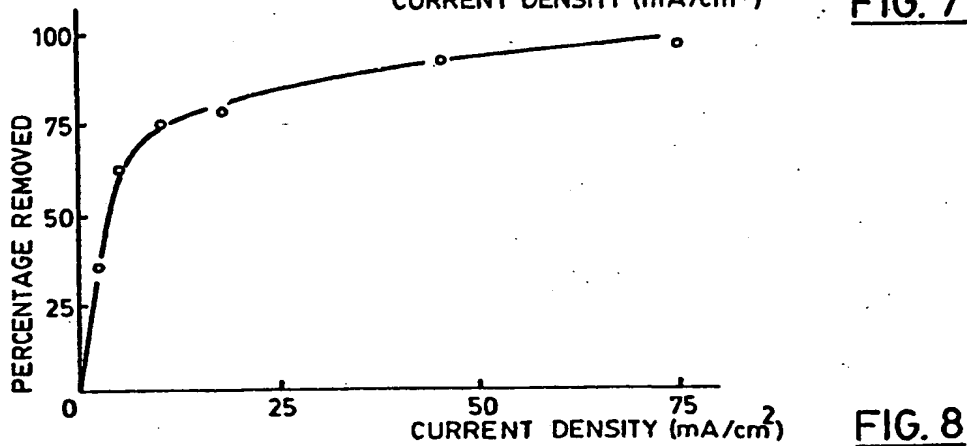
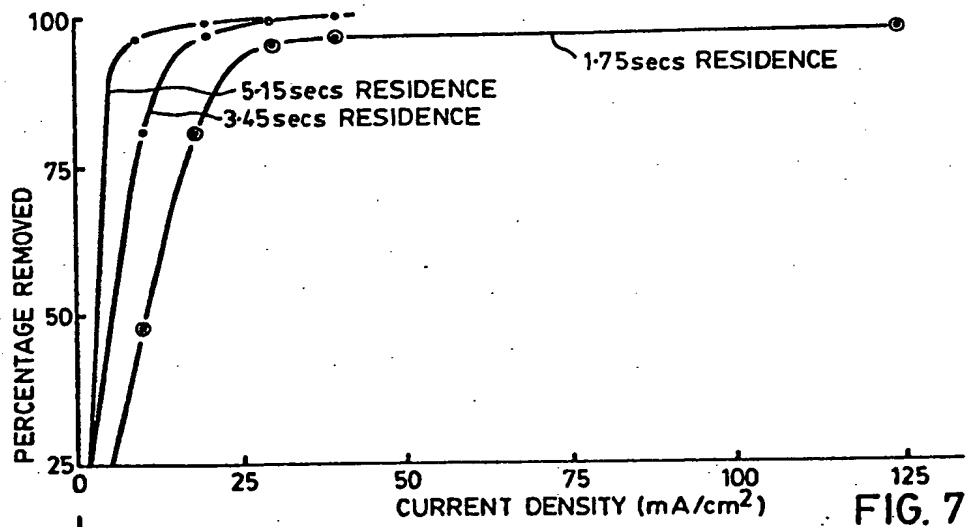
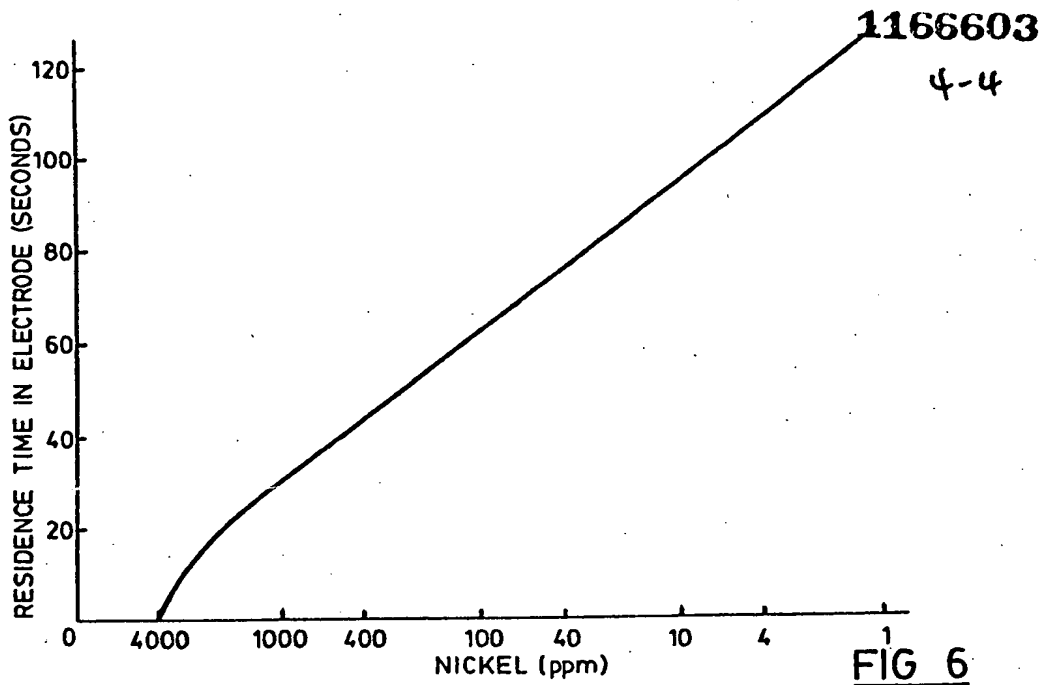
FIG. 3

Winn, Jones & Son

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Harris, Rogers & Smith
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